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The Role of Zinc Sulfate in Peach Sprays

By K. J. Kadow and
H. W. Anderson

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Urbana, Illinois April, 1935

Publications in the Bulletin series report the results of investigations made by or sponsored by the Experiment Station

The Role of Zinc Sulfate in Peach Sprays

By K. J. Kadow, Assistant Pathologist in Horticulture, and
H. W. Anderson, Chief in Pomological Pathology*

INTRODUCTION

PRIOR to the year 1932 the standard summer insecticidal spray for peaches in Illinois was acid lead arsenate and lime, with a suitable fungicide added at various times during the season for the control of peach diseases, especially brown rot. Under certain environmental conditions heavy losses, as a result of injury to trees and fruit, were sustained by growers following this schedule. Attempts to evaluate losses caused respectively by spray injury, bacterial spot, and brown rot were difficult because of an apparent interrelationship of the troubles, especially between spray injury and the bacterial spot disease.

Observations in 1928, by the junior author, of the apparently successful use of zinc sulfate as a peach-spray ingredient in the experimental plots of the U. S. Department of Agriculture at Vincennes, Indiana, led to an intensive study of this material under Illinois conditions. In 1929 experiments were begun[3*] at Carbondale, Illinois, which have since been continued and expanded.

In the various reports of Roberts *et al* [52-60*] important fungicidal, bactericidal, and stimulating powers have been attributed to zinc sulfate as applied in their experiments. Applications of similar schedules under Illinois conditions led to the belief that much of the supposed effect of this chemical might require a different interpretation than that given by the original workers. In order to ascertain, if possible, the exact role of zinc sulfate as a fungicide and bactericide, as a stimulant to peach growth, and as a corrective of spray injury, the studies herein reported were begun.

*The writers acknowledge their indebtedness to W. A. Ruth, Professor of Pomological Physiology, University of Illinois, for assistance and advice on the chemical aspects of this problem. They are also indebted to P. L. Hibbard, of the University of California, for permission to include herein his zinc analyses of peach tissue.

*These numbers refer to literature citations on pages 249 to 252.

The chemicals used in the experiments were ordinary commercial brands unless otherwise stated. The lime, $Ca(OH)_2$, was purchased from the Lehigh Lime Company and was a high-grade hydrated type. The zinc sulfate, granular form $ZnSO_4.7H_2O$, was secured from the Grasselli Chemical Company. Sherwin-Williams acid lead arsenate, $PbHAsO_4$, was used thruout. In all the field experiments ordinary pond water was used to make up the mixtures, except at Urbana, where tap water was available. All the waters were hard and varied considerably in chemical composition. The sprays were applied with commercial spray rigs under approximately 300 pounds pressure.

ZINC SULFATE AS A FUNGICIDE

Since the introduction of self-boiled lime sulfur mixture by Scott[63*] in 1907 as a safe peach fungicide, a number of other fungicides for peaches have appeared on the market. Practically all contain sulfur in some form as their active ingredient and give satisfactory control of brown rot (*Sclerotinia fructicola* (Wint.) Rhem.) and scab (*Cladosporium carpophilum* Thum), the two outstanding fungous diseases of peaches in Illinois, but are not satisfactory for the control of bacterial spot (*Phytomonas pruni* (E.F.S.) Bergey *et al*).

In an attempt to control bacterial spot, Roberts and Pierce[52-60*] started experiments in 1925 which led to the introduction of zinc sulfate into the peach spray program.[a] Considering the material strictly in a fungicidal capacity, Roberts and Pierce[56*] made the following statements: "The results are fairly consistent and indicate that zinc-lime can be depended upon to control at least moderate outbreaks of scab," and "Results in the control of brown rot are not conclusive but indicate that zinc-lime will check and probably control the disease."

After one season of experimentation Anderson and Thornberry[3*] stated that zinc-bordeaux gave only fair control of brown rot, but they also indicated that the results were probably not very significant because of an apparent relation between brown rot infections and some type of mechanical or insect injury to the epidermis of the fruit.

Zinc Sulfate as a Control for Peach Scab

Altho experiments with peach sprays have been conducted yearly in Illinois since 1929, the first significant field results with zinc sulfate

[a]The relation of this chemical to bacterial spot control will be discussed later in this paper (see pages 214-221).

as a fungicide were obtained in the 1933 plots at Irvington, Illinois, where some very striking information in relation to peach scab was secured.

The Irvington experiment was conducted in the E. C. Riechman orchard, chosen for several reasons: the trees were well pruned and cultivated; the soil type, and consequently tree size and vigor, were remarkably uniform; general tree vigor was rather low, because the owner, discouraged by repeated crop failures resulting from late spring frosts and winterkilling of fruit buds, had not maintained proper soil fertility; bacterial spot was present and usually caused severe defoliation; peach scab, too, was usually present but was seldom severe. All these conditions in combination made the Riechman orchard especially suitable for the spray tests.

Each plot except Plots 1 and 4 received five summer sprays at two-week intervals. Only four sprays were applied to Plot 4, the fifth being omitted. Plot 1, the absolute check, received no spray or dust. The sprays applied are described in Spray Schedule No. 3 (page 255) and the results of the experiment are given in Table 1.

An examination of Table 1 shows that of the 2,000 fruits inspected on Plot 1 (the absolute check) 462, or 23.1 percent, were infected with peach scab. No peach was recorded as diseased unless it showed three or more scab lesions.

Five applications of zinc sulfate and lime and of combinations of zinc sulfate - lime and lead arsenate reduced infections to a range of 1.8 to 2.6 percent. The lead-lime spray, however, gave equally successful control, reducing infections to 1.2 percent (Plot 2). Thus the addition of zinc sulfate to lead-lime sprays appeared to have no advantage over lead-lime alone in the control of peach scab. The results herein obtained with zinc sulfate and lime substantiate those reported by Roberts and Pierce,[56*] who secured control of peach scab by the use of that combination on individually sprayed branches. The only check used by Roberts and Pierce, however, was unsprayed branches. It is probable that lead-lime sprays would have shown the same control. It is evident from these tests, however, that from a practical standpoint the addition of zinc sulfate to the lead-lime spray would be useless if it had no other function than the control of peach scab.

Attempts to study the effects of various spray mixtures on the germination of spores of the peach scab organism in laboratory tests were unsuccessful because of the lack in uniformity of spore germination.

TABLE 1.—FRUIT RECORDS OF SPRAYING EXPERIMENT[a] AT IRVINGTON,[b] ILLINOIS
(Examination of fruit August 7, 1933, at harvest)

Number of fruit examined	Scab	Bacterial spot	Brown rot	Spray injury	Drops[c] (10 trees)
Plot 1: Absolute check (no spray or dust)					
2000	462	118	4	0	43
Fruit color a light yellowish-green. About twice as much foliage present as on Plot 2. Leaves generally deep green and in good condition.					
Plot 2: Lead, 3 pounds; lime, 6 pounds; water, 100 gallons					
2000	24	125	10	1062	852
Fruit highly colored; red on exposed, weathered side. Sixty percent leaves off; remaining leaves show much injury. See Fig. 6 for typical fruit injury.					
Plot 3: Zinc, 8 pounds; lime, 8 pounds; lead, 3 pounds; water, 100 gallons					
2000	52	108	4	198	66
Fruit color slightly more reddish than check (Plot 1). The fruit injury never more than blackish discoloration; no fruit cracking. Leaves in good condition; very little spray injury.					
Plot 4: Zinc, 4 pounds; lime, 8 pounds; lead, 3 pounds; water, 100 gallons					
2000	36	114	5	284	140
Fruit moderately colored; considerable red. Small amounts of cracking on some injured fruits. Leaf injury; leaf fall moderately light.					
Plot 5: Zinc, 8 pounds; lime, 8 pounds; water, 100 gallons					
2000	41	119	7	0	52
Fruit and leaf condition about same as on Plot 1, the check.					

[a]For spray schedule see No. 3, page 255, Appendix.
[b]Experiment carried out at E. C. Riechman orchard, Irvington, Ill. Trees in poor vigor. Bacterial spot generally severe, causing considerable defoliation at harvest time. Peach scab general, but brown rot very scattered. Five sprays applied at 2-week intervals (beginning with shuck spray), except in Plot 4, which received only four sprays, the last being omitted. No late-season sprays or dusts were applied this season.
[c]Drops were not included in the 2,000 fruits examined in each plot. They represent the number present under 10 trees selected at random.

Zinc Sulfate as a Control for Brown Rot

Attempts to secure field data on brown rot control by zinc sulfate - lime sprays have been made yearly in Illinois since 1929, but no significant results have been obtained. Those listed in Table 1 are typical.

In recent years laboratory testing of chemicals to determine their toxic properties has been steadily gaining in accuracy. Methods have become standardized to such an extent that the results may be depended upon to serve as an index of the field performance of the

material tested. This is especially true in the investigation of the toxic properties of various chemicals on the brown rot organism, the fungus most generally used in determining the comparative values of spray materials. For these reasons it was possible to study the fungicidal value of zinc sulfate in the laboratory (Table 2). The technic employed was essentially the same as that used by McCallan.[37*]

Because the brown rot fungus is easily cultured and its conidia germinate readily in water, it lends itself very effectively to laboratory fungicidal tests. It was found in the present investigation that the addition of 1 percent sucrose to sterile distilled water gave practically 100 percent germination of conidia from cultures 7 to 12 days old. This finding seems to be in agreement with that reported by Wilcoxon and McCallan,[74*] altho in their studies aqueous plant extracts were used. Doran[13*] points out that spores of other fungi may exert an injurious effect upon the germination of spores of the fungus being tested; consequently only pure cultures of brown rot and sterile distilled water were used in these studies. Wallace *et al*[73*] and McCallan[37*] have demonstrated that, because of oxygen limitations and staling effect, there is a limit to the number of spores that will germinate in a given amount of water. McCallan[37*] obtained best germination of brown rot spores at a concentration of 20-50 per microscopic field of 1,575 microns diameter, with the spores suspended in distilled water, and at a temperature between 21 and 25.5° C. It was found by the present writers that practically 100 percent germination resulted if the spore concentration was not higher than 125 spores per microscopic field of 1,898 microns diameter. All the laboratory tests herein reported were carried out at temperatures ranging between 22 and 25° C.

Another important point which must be considered is described by McCallan and Wilcoxon[38*] as "the form of the toxicity surface." In an attempt to minimize variation caused by this factor, all slides in the present study were sprayed with a very fine mist from an atomizer. The slides were sprayed until the tiny droplets began to coalesce. The consistency of replicate tests indicates that this precaution was well worth while. One set of slides was treated and allowed to dry for 24 hours before the brown rot fungus was added. Another set was similarly treated but allowed to dry and weather in the laboratory for ten days before the brown rot fungus was added. Both of these experiments were duplicated.

Particular care was exercised when adding the brown rot spore suspension to the treated slides to get the areas covered by the bases

TABLE 2.—INFLUENCE OF CHEMICALS ON SPORE GERMINATION TESTS OF BROWN ROT

(Cultures 7 to 10 days old. Spores suspended in 1 percent sucrose dissolved in sterile distilled water. Three check slides placed in each damp chamber containing specially treated slides.)

Proportions[a]	Number of conidia per microscopic field		Percentage of germination		Germ tube length in microns	
	Slides dried 24 hours	Slides weathered 10 days	Slides dried 24 hours	Slides weathered 10 days	Slides dried 24 hours	Slides weathered 10 days
			$ZnSO_4.7H_2O$			
2–100	100	100	50	50	5–20	10–15
	110	110	50	75	5–20	10–25
4–100	90	130	10	25	5–20	5–15
	100	100	15	20	5–20	10–40
6–100	100	110	5	11	5–15	1–20
	120	110	8	15	5–15	1–20
8–100	100	140	0	Trace	0	2
	100	130	0	0	0	0
10–100	90	120	0	0	0	0
	110	100	0	0	0	0
12–100	110	100	0	0	0	0
	100	90	0	0	0	0
Checks	100	100	100	99	100–1000	100–1000
	90	100	100	99	100–1000	100–1000
	100	110	100	99	100–1000	100–1000
			Kopper's flotation sulfur (wettable)			
2–100	110	...	1	...	5–100	...
	100	...	1	...	5–100	...
4–100	100	...	0	...	0	...
	90	...	0	...	0	...
6–100	100	...	0	...	0	...
	110	...	0	...	0	...
Checks	110	...	99	...	100–1000	...
	110	...	100	...	100–1000	...
	100	...	100	...	100–1000	...
			Lime (hydrated)			
2–100	...	100	...	95	...	100–300
	...	90	...	90	...	10–250
4–100	...	100	...	90	...	100–250
	...	100	...	80	...	100–200
6–100	...	110	...	85	...	75–250
	...	100	...	85	...	75–250
8–100	...	100	...	85	...	75–250
	...	90	...	80	...	75–250
10–100	...	110	...	80	...	50–200
	...	90	...	80	...	50–200
12–100	...	120	...	60	...	10–100
	...	100	...	80	...	10–100
16–100	...	110	...	50	...	10–100
	...	100	...	50	...	10–100
Checks	...	140	...	98	...	100–1000
	...	100	...	100	...	100–1000
	...	120	...	99	...	100–1000
			Zinc sulfate – lime			
2–2–100	100	110	90	85	50–300	100–250
	95	95	95	85	50–300	100–250
2–4–100	100	110	90	80	50–250	100–200
	110	100	80	80	50–200	100–200
4–4–100	90	120	40	45	25–200	20–150
	110	90	40	40	25–200	20–150
4–8–100	100	110	35	45	10–200	20–150
	130	100	30	45	10–200	20–150

TABLE 2.—*Concluded*

Proportions[a]	Number of conidia per microscopic field		Percentage of germination		Germ tube length in microns	
	Slides dried 24 hours	Slides weathered 10 days	Slides dried 24 hours	Slides weathered 10 days	Slides dried 24 hours	Slides weathered 10 days
Zinc sulfate – lime—*concluded*						
8–8–100	100	110	10	5	5–100	10–100
	90	100	15	7	5–100	10–100
8–16–100	...	90	...	5	.....	10–100
	...	100	...	5	.....	10–100
12–12–100	110	120	10	3	5–100	10– 70
	100	100	8	5	5–100	10– 70
Checks	100	100	100	98	100–1000	100–1000
	90	110	99	100	100–1000	100–1000
	100	100	100	99	100–1000	100–1000
Zinc sulfate – lead arsenate – lime						
2–3–6–100	100	100	8	5	5– 75	5– 40[b]
	110	100	10	8	5– 75	5– 40
4–3–8–100	90	120	4	4	5– 40	5– 40
	90	90	5	5	5– 40	5– 40
8–3–8–100	100	120	3	5	5– 40	5– 25
	90	100	3	3	5– 40	5– 25
Checks	100	100	100	99	100–1000	100–1000
	110	110	99	100	100–1000	100–1000
	130	130	98	100	100–1000	100–1000
Lead arsenate – lime						
2–4–100	100	140	10	8	5–100	5–50
	100	100	12	10	5–100	5–50
3–6–100	100	110	8	5	5–25	5–25
	90	100	8	5	5–25	5–25
3–8–100	110	120	8	5	5–25	5–25
	100	90	8	2	5–25	5–25
Checks	90	130	100	99	100–1000	100–1000
	120	110	100	100	100–1000	100–1000
	100	120	100	98	100–1000	100–1000
Copper sulfate – lime						
.4–.6–100	...	...	.5	...	10– 20	...
.8–1.2–100	...	...	0	...	0	...
2–3–100	...	...	0	...	0	...
4–6–100	...	...	0	...	0	...
Checks	...	...	100	...	100–1000	...
	...	...	100	...	100–1000	...
	...	...	99	...	100–1000	...
$CuSO_4.5H_2O$						
grams per cc.						
1–1000	100	110	0	0	0	0
	120	100	0	0	0	0
1–2000	100	120	85	25	10–250	10–150
	100	100	80	25	10–250	10–150
1–3000	110	90	100	100	100–2000[c]	100–1700[c]
	90	140	100	100	100–2000	100–2000
1–4000	90	120	100	100	100–2000	100–1700
	100	100	100	100	100–2000	100–1700
Checks	100	100	99	99	100–1000	100–1000
	110	110	100	100	100–1000	100–1000
	100	120	99	99	100–1000	100–1000

[a]All materials expressed as pounds per 100 gallons of water unless otherwise stated.
[b]Microscopic character of the germ tubes practically identical in this series to the germ tubes in the lead-lime series.
[c]Note apparent stimulation.

of the drops equal. Two drops of the spore suspension were placed at a given point on the treated slides, and each slide contained three such points. These "points" will be referred to thruout this discussion as *drops*. The number of spores per microscopic field was calculated by actually counting five to ten fields, or portions of fields, for each drop, and then computing the average for all readings for the three drops on a given treated slide. Approximately the same number of counts were made to determine the percentage of germination. The figures listed in Table 2, showing results of toxicity studies of certain chemicals on brown rot spores (*Sclerotinia fructicola* (Wint.) Rehm.), represent an average of all readings. Readings were made 24 hours after the spore suspensions had been added to the slides. Each series of slides representing a given treatment along with three check slides were placed in individual damp chambers after the spore suspension drops were added.

Conclusions Regarding Zinc Sulfate as a Fungicide

As a fungicide, zinc sulfate evidently possesses no particular advantages over lead arsenate - lime. Neither in the field tests with peach scab, nor in the laboratory tests with brown rot did zinc sulfate - lime with or without lead arsenate show any superiority over lead arsenate - lime alone. It is evident, however, that either the lime-lead or the lime-lead-zinc spray is adequate for commercial control of peach scab under average conditions. Whether either type of spray would control a severe outbreak of scab has not as yet been demonstrated. Likewise, altho zinc sufate ($ZnSO_4.7H_2O$) has a slightly toxic effect on the germination of brown rot spores in laboratory tests, it seems very unlikely that zinc-lime sprays could be relied upon to control brown rot under field conditions. Satisfactory field tests must be made, however, before this point can be definitely determined.

In general, if applications are to be made primarily for peach scab or brown rot control, there seems to be little justification for the use of zinc sulfate - lime. Sulfur is a much more effective fungicide.

ZINC SULFATE AS A BACTERICIDE

Zinc sulfate - lime was originally introduced as a peach spray by Roberts and Pierce[52*] and is claimed in their most recent article[56*] to be an effective bactericide in controlling the peach bacterial spot disease caused by *Phytomonas pruni* (E.F.S.) Bergey *et al.* The following experiments with zinc sulfate and zinc sulfate spray combina-

tions were initiated to determine, if possible, whether recommendations for the commercial usage in Illinois of zinc sulfate sprays applied specificially for the control of *P. pruni* are justified.

Field Tests With Zinc Sulfate as a Bactericide

Data on bacterial spot were obtained from experiments carried on at three orchards located at Carbondale, Irvington, and Olney, Illinois.

The primary purpose of the experiments conducted in 1932 at Carbondale, at the C. J. Thomas orchard, was to study the effects of zinc sulfate on stimulation and arsenical injury, but observations were taken also on bacterial spot. The trees of this orchard, of the Hale variety, were in fine vigor, with a moderate crop of fruit. Several interesting observations were made in regard to leaf infections, but records of the fruit condition at harvest were of no significance because of the lack of uniform infection. All plots in this orchard were maintained in duplicate except a few upon which severe injury was expected.

In 1933, data on bacterial spot were obtained from experiments conducted at Irvington, Illinois, in the E. C. Riechman orchard described above (page 209), and at the University orchard at Olney, Illinois. The University orchard, so far as experiments herein discussed are concerned, was composed of five-year-old Elberta and Gage varieties, was in good general vigor, and usually had a moderate infestation of bacterial spot. Details of the spray schedules applied in these experiments are given in the Appendix (pages 254-255).

The most conclusive results of the three experiments were obtained in the Irvington orchard. It appears that the low state of vigor of this orchard permitted serious injury from bacterial spot on both the leaves and the fruit. Often when both the bacterial spot disease and spray injury are present on a given leaf, it is very difficult, if not occasionally impossible, to determine accurately the cause of the necrotic spotting. In order to minimize the error introduced by this factor, frequent miscroscopic examinations of doubtful cases were made, but in spite of this precaution undoubtedly some error exists in the records involving these interrelationships. The results of these experiments as they pertain to *P. pruni* are given in Table 3.

One important fact which the records in Table 3 do not indicate,—namely, that zinc sulfate in spray mixtures prevents the cracking and corky tissue formation which generally results when *P. pruni* infected fruit is sprayed with lead arsenate - lime sprays,—is brought out quite effectively in Fig. 1, which shows typical bacterial spot injury on two

TABLE 3.—RESULTS OF SPRAYING EXPERIMENTS FOR THE CONTROL OF BACTERIAL SPOT ON PEACHES AT CARBONDALE, IRVINGTON, AND OLNEY, ILLINOIS

Spray schedules[a]		Plots	Location of experiments	Year	Variety	Leaf fall	Bacterial spot	
Materials used	No.						Leaves	Fruit
						perct.	*perct.*	*perct.*
Absolute checks (no sprays)	1	C1, 17a	Carbondale	1932	Hale	5.1	8	....
	3	1	Irvington	1933	Elberta	7.9	25	5.9
	2	1	Olney	1933	Elberta	6.1	8	....
	2	1	Olney	1933	Gage	4.9	5	....
Lead-lime	1	7, 18	Carbondale	1932	Hale	32.4	19	....
	3	2	Irvington	1933	Elberta	28.0	16	6.25
	2	2	Olney	1933	Elberta	22.1	3	....
	2	2	Olney	1933	Gage	19.8	4	....
Zinc-lime-lead	1	1, 13	Carbondale	1932	Hale	10.5	11	....
	3	3	Irvington	1933	Elberta	8.9	21	5.4
	2	3	Olney	1933	Elberta	9.8	10	....
	2	3	Olney	1933	Gage	8.1	4	....
Zinc-lime	1	10, 19	Carbondale	1932	Hale	5.1	9	....
	3	5	Irvington	1933	Elberta	8.8	22	5.95

[a]Details of the sprays applied are given in the spray schedules in the Appendix, page 254-255.

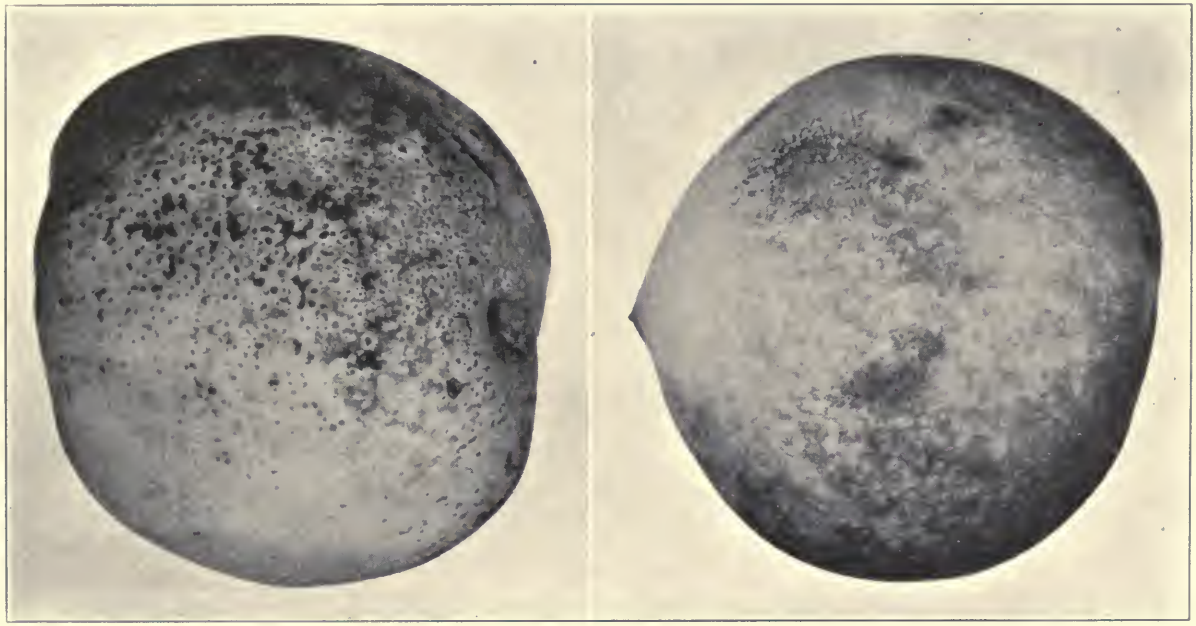

FIG. 1.—EFFECTS OF ZINC-LIME AND LEAD-LIME SPRAYS ON BACTERIAL LESIONS ON PEACHES

(Left) Typical bacterial spot injury on fruit sprayed with lead arsenate - lime mixtures. *(Right)* Bacterial lesions on fruit sprayed with zinc sulfate - lime. Lesions of the character shown here were also typical of those found on fruit from the absolute checks and from trees sprayed with mixtures of zinc sulfate, lead arsenate, and lime.

peaches, one sprayed with five applications of lead-lime and the other with five applications of zinc sulfate - lime. The type of lesion on the peach sprayed with zinc-lime was also typical of bacterial spot on fruit sprayed with a 3-8-8-100 lead-lime-zinc mixture. Application of lead-lime sprays tended to aggravate the injury ordinarily resulting from bacterial spot. On unsprayed fruit with the same degree of infection, the cracking and corky tissue formation was never so severe as on fruit sprayed with lead-lime, altho some severe cracking on unsprayed checks was not uncommon. On the other hand, whenever sprays applied to the peach had zinc sulfate as one of the ingredients, the *P. pruni* fruit lesions were seldom more than light flecks with no visible cracking. The zinc sulfate apparently does not reduce the actual number of bacterial spot infections, but the character of the lesions is greatly influenced. While this difference may seem of little importance, it often directly affects the market value of the fruit.

Laboratory Experiments With Zinc Sulfate as a Bactericide

In order to test further the bactericidal powers of zinc sulfate in relation to *P. pruni,* investigations were made in the laboratory. The method used in these tests, altho somewhat different from the standard phenol coefficient method, was followed because it simulates more closely actual field conditions than does the standard method. It is not new, but has been used for similar purposes in this laboratory since 1927. It must be clearly understood, however, that these studies are entirely relative and should be interpreted accordingly.

The materials to be tested were weighed and made into stock solutions of any desired concentration. Sterile distilled water was used to make the solutions. A bacterial suspension of *P. pruni* was made by placing the desired amount of bacteria in sterile distilled water. The cultures of *P. pruni* used in these tests were usually 72 hours old. Bacterial suspensions were adjusted to yield, under the procedure subsequently described, about 200 colonies per petri dish of 9½ centimeters diameter. Dilutions were made by transferring certain quantities of the stock solution to sterilized test tubes containing sufficient sterile distilled water to make the dilution desired. After a series of dilutions were prepared, one drop of the bacterial suspension was added to each 1 cc. of each dilution. The dilutions were shaken frequently to insure a complete breaking up of the slimy bacterial masses generally produced by *P. pruni.* By disintegrating these slimy masses into individual cells, or into very small clumps of bacteria, the toxic or inhibitory substance in the materials being tested

could more readily come into contact with each individual bacterium. The materials were allowed to act on the bacteria for ten minutes at a laboratory temperature of 21 to 22° C. The tubes were thereupon poured and incubated at 25° C. for four days. Checks were run to determine the sterility of the distilled water, the media, and the various chemicals used in the tests. Checks were also run to determine whether the small amounts of the toxic materials transferred to the media had any effect upon the growth of the bacteria. No harmful effect was observed in any instance. The results of these tests are listed in Table 4, and are very similar to those obtained by Anderson and Thornberry.[4*]

An examination of Table 4 reveals that lime alone is more toxic to growth of *P. pruni* in culture than is zinc sulfate, lead arsenate, or any combination of the three. This, of course, may not be true under field conditions. Zinc sulfate at best is but a mild bactericide, as may readily be seen by comparing its action in the preceding laboratory tests with that of copper sulfate.

Field Observations of Zinc Sulfate as a Bactericide

In addition to the data presented in the preceding paragraphs, observations have been made in many orchards under a variety of cultural conditions and spray programs in order to determine the effect of zinc sulfate - lime sprays on the control of *P. pruni.* All these observations lead to the same conclusions, namely, that so far as the actual number of infections by *P. pruni* are concerned, zinc sulfate - lime has no measurable effect. In other words, there are actually as many diseased fruits, leaves, and twigs on plots sprayed with zinc sulfate - lime as on absolute checks or on plots sprayed with other materials.

Likewise, a difference in tree vigor does not seem to influence materially the actual number of infected tree parts. Vigor does, however, exert a marked influence on the amount of defoliation and, therefore, indirectly on general tree condition. If orchards in a given state of vigor are sprayed with lead arsenate - lime, a great deal of defoliation usually occurs, especially on trees of low vigor. If *P. pruni* is infecting the trees of these orchards, considerable additional defoliation will result. This appears to be due, at least in part, to additional spray injury facilitated by the lesions caused by the bacterial spot organism. The point is well illustrated in Fig. 1.

The above discussion is not meant to imply that *P. pruni* does not oftentimes cause severe defoliation, but, instead, that healthy vigorous

TABLE 4.—TOXICITY OF VARIOUS CHEMICALS OR CHEMICAL MIXTURES TO BACTERIAL SPOT

Materials tested	Number of replications	Dilution range[a]	Highest dilution toxic	Comments
Zinc sulfate ($ZnSO_4.7H_2O$)	3	1-50 to 1-800	1-50	Ten colonies on 1 plate.
	2	1-50 to 1-1000	1-50	No growth.
	1	1-100 to 1-1000	0	Many colonies at 1-100.
	1	1-20 to 1-200	1-100	Eight colonies on 1 plate.
Lead-lime	3	⅜-1-50 to ⅜-1-200	⅜-1-50	Five colonies on 1 plate, 2 on another.
Lead arsenate ($PbHAsO_4$)	3	1-200 to 1-300	0	Many at 1-200.
Lime ($Ca(OH)_2$)	3	1-100 to 1-1000	1-100	Three colonies on 2 plates at 1-100.
	2	1-50 to 1-800	1-100	Two colonies on 1 plate.
Zinc-lime-lead	3	1-1-⅜-50 to 1-1-⅜-200	1-1-⅜-50	Plates had 1, 20, and 28 colonies respectively.
	3	1-1-⅜-50 to 1-1-⅜-200	0	All plates had many colonies.
	3	1-1-⅜-50 to 1-1-⅜-200	0	One plate had 9 colonies, others many.
Zinc-lime	3	1-1-50 to 1-1-200	1-1-50	One plate had 1 colony.
	3	1-1-50 to 1-1-200	0	All plates had many colonies.
	3	1-1-25 to 1-1-100	1-1-25	Two plates at 1-1-50 had 69-47, the other only 1.
Copper sulfate ($CuSO_4.5H_2O$)	3	1-100 to 1-1000	1-1000	No growth at 1-1000.
	3	1-500 to 1-20,000	1-20,000	Grayish-white bacteria present at 1-20,000; no *P. pruni*.
Checks	2	Media and petri dishes	.....	No growth.
	2	Sterile distilled water used	.....	No growth.
	3	*P. pruni* cultures used	.....	Apparently pure, about 200 colonies per plate.
	2	Lime	.....	A few grayish-white bacteria.
	2	Lead arsenate	.....	A few fungous colonies.
	2	Zinc sulfate	.....	A few grayish-white bacteria.
	2	Copper sulfate	.....	No growth.

[a]Dilutions expressed as grams in cubic centimeters. Commercial strength recommended: zinc-lime 1-1-100; zinc-lime-lead 1-1-⅜-100; lime-lead 1-⅜-100.

trees are generally as badly infected as trees in a low state of vigor, and that the real difference lies in the fact that the vigorous trees retain their infected parts while trees in low vigor drop them prematurely. This observation also applies to the amount of injury done by lead arsenate - lime sprays in any given season. Indirectly defoliation is often responsible for other troubles, such as winter injury and the like, which in a long-time experiment often make differences very outstanding.

Conclusions Regarding Zinc Sulfate as a Bactericide

Thus field observations, supported by field studies and laboratory toxicity tests, indicate in general that zinc sulfate ($ZnSO_4.7H_2O$), however used, is a very poor bactericide. Zinc sulfate - lime sprays applied specifically for the control of *P. pruni* are probably of no commercial value.

EFFECT OF ZINC ON GROWTH OF PEACH

It is now a well-established fact that many plants need as nutrients, or are stimulated by, some of the rarer elements. Very little is at present known of the specific requirements for plants in general. It is certain, however, that not all plants require the same chemicals.

Review of Literature

With constant improvement in physiological technic and analytical methods, rare elements required for plant growth are constantly coming to light. In 1927 Brenchley[6*] contributed a very interesting review on rare elements and their relation to plant growth.

In a recent article by Lutz[33*] the literature which pertains to the recovery of zinc from plants is reviewed. He states:

"Zinc has been found, then, in all plant and vegetable materials that have been analyzed, and in amounts often comparable to those in which iron occurs. It has been suggested, because of this fact, that zinc, as a normal constituent, is necessary to plant life and that it probably plays some important but as yet unknown part in vegetable metabolism."

Several papers on this subject have appeared since Lutz published his findings and literature review, all of which add additional weight to the above quotation. It does not necessarily follow, however, that because zinc is recovered from plant ash it is a necessary or even a desirable element for plant growth. This point must be proved by properly conducted nutritional experiments.

In 1869 Raulin[49*] found that zinc was a necessary element for

the development of *Aspergillus niger.* Since 1869 a great many workers have experimented on the relation of zinc to various fungi and, in the main, have found that it is necessary for or stimulates their development. The most recent of these articles are by McHargue and Calfee,[40,41*] Niethammer,[44*] Roberg,[50,51*] and Porges.[48*]

The favorable effect of zinc on the development of plant life is not confined to the fungi. In articles by Maze,[34,35,36*] Sommer and Lipman,[68*] Sommer,[66,67*] and McHargue and Shedd,[39*] the fundamental nature of zinc in relation to the growth of several chlorophylous plants is shown. In 1932 Haas[22*] reported that additions of zinc nitrate ($Zn(NO_3)_2.6H_2O$) to culture solutions improved the quality but not the quantity of the growth of citrus. Roberts and Pierce[56*] observed a deeper green color in foilage and general tree improvement as a result of spraying peach trees, under field conditions, with a zinc sulfate - lime mixture. Falkenberg[15*] found that the dry weight of tomatoes, beans and peaches was reduced by applications of zinc-lime sprays. He contended that the chlorophyl per unit area was increased in tomato and bean leaves, but that peach foliage was only slightly affected, if at all. It must be remembered that the plants with which he worked were growing in soil that undoubtedly supplied the zinc requirements of the plants in question.

Chandler,[8*] Chandler *et al,*[9*] and Johnston[30*] report that little-leaf, or rosette, of various fruit trees may be cured by applications of zinc sulfate. These applications may be made directly to the soil, thru holes in the trunks, or as sprays to the leaves. Finch,[16*] Alben *et al,*[1*] and Finch and Kinnison[17*] present conclusive evidence that rosette of pecans can be cured with proper amounts of zinc. Mowry and Camp[43*] report that bronzing of Tung trees may be entirely corrected by applications of zinc sulfate to the soil or leaves. These workers also list other troubles which were corrected by applications of zinc sulfate. That these diseases are physiological in nature and are due largely to the lack of sufficient zinc for normal metabolism now appears certain. In a recent article by Drinker and Collier[14*] several opinions as to the significance of zinc in the living organism are reviewed. Inclusion here of a summary of these opinions does not seem justifiable, as in the words of Sommer and Lipman[68*] with regard to all rare elements: "We have not even a clue relative to the manner in which these elements function in cell metabolism." It now appears to be well established that the elements which may be required only in extremely small amounts are truly essential in many cases and are no longer to be regarded as mere stimulants.

In investigating rare elements in relation to plant growth, few workers have realized the necessity for extremely careful technic. Sommer[66*] found, when studying the effect of zinc, that ordinary "mason" jars liberated enough to influence her results, and that dust in the air did likewise. She also reported that "C.P." chemicals were not pure enough for such detailed studies, and that when they were recrystallized plants would not grow in them. In this connection the present writers found by spectroscopic analysis that most of the "C.P." chemicals used in a nutrient solution, described later, contained zinc impurities. Attempts to grow peach seedlings in this solution after the chemicals were purified failed, but when the solution was made of ordinary "C.P." chemicals the seedlings grew very nicely. Thus it may be seen that extreme care must be exercised if a true picture of this important problem is to be obtained.

The distribution of zinc in any given plant seems to vary considerably. Javillier and Imas[29*] found that in certain grain crops the embryo had 22 times as much zinc as was present in the endosperm. According to Bertrand *et al,*[5*] leaves seem to have the largest amount of zinc. It is also evident that the amount of zinc present in any given species of plants varies a great deal. There is undoubtedly a rather direct relation between the amount of zinc present in plants and the amount of soluble zinc present in the soil on which they grow.

Investigations of zinc in relation to peach growth were undertaken to answer the following questions: (1) Is zinc present in healthy peach tissue? (2) Does zinc influence the growth of peaches in nutrient solutions? (3) What is the influence of zinc sulfate - lime sprays applied to the peach under Illinois field conditions?

Presence of Zinc in Healthy Peach Tissue

Most methods for the recovery of small amounts of zinc, according to the experience of the present writers, are not suitable when many other elements are present, as in ashed peach leaves. Consistent results were obtained, however, by following the iodometric titration method of Lang[32*] as modified by Hibbard.[26*]

The peach leaves analyzed were selected from trees growing at Urbana on Carrington silt loam soil. The analyses (Table 5) were made during the 1934 growing season: the first lot of leaves had never been sprayed or dusted (Plot 1), whereas the second had received five sprays of 8 pounds of zinc sulfate, 8 pounds of hydrated lime, and 3 pounds of lead arsenate to 100 gallons of water (Plot 2). All material analyzed was treated in the following manner:

1. Washed thoroly with ordinary distilled water.
2. Washed in a weak solution of distilled HCl acid (10 percent for 5 minutes).
3. Rinsed with conductivity water.
4. Third step repeated.
5. Dried at 105° C. for 24 hours.
6. Incinerated in a muffle furnace at 700 to 800° C. until all carbon was completely oxidized (usually 2 to 3 hours).
7. Material carefully weighed and analyzed by iodometric titration.

TABLE 5.—ZINC CONTENT OF LEAVES COLLECTED FROM HEALTHY PEACH TREES AT URBANA, ILLINOIS, DURING THE 1934 GROWING SEASON

Plot	Treatment	Zinc present	
		P.p.m. (dry weight)	Milligrams per gram of ash
1.....	Absolute check (no sprays or dusts).....	23	.35
		17	.25
		18	.28
		15	.23
		14	.22
2.....	Five applications of zinc-lime-lead 8-8-3-100[a].....	25	.37
		20	.30
		23	.35
		19	.28
		16	.24

[a]Tap water.

The finding of zinc in healthy peach tissue in these tests is confirmed by experiments by P. L. Hibbard, University of California, who analyzed for zinc content peach tissue from various parts of the country, including a sample from Plot 1 at Urbana, and who has granted permission to include in the present chapter a report of the results of his analyses (Table 6). His findings from the material sent from Urbana were secured by measuring the turbidity of zinc ferocyanide by means of a photoelectric cell, and indicate considerably smaller amounts of zinc than those listed in Table 5. Since the material used was the same, the difference in results may be due, at least in part, to the fact that different methods were employed.

The results of analyses made at California and at Illinois indicate that zinc is always present in healthy peach tissue. It appears, also, that when peach trees are sprayed with zinc sulfate mixtures a slight penetration of the leaves is effected by the zinc.[a] This penetration

[a]In this study lead and arsenic were also recovered from within the leaves which had been sprayed as in Plot 2, Table 5.

TABLE 6.—ZINC FOUND IN PEACH LEAVES AND TWIGS, UNIVERSITY OF CALIFORNIA STUDY

(Samples taken by W. H. Chandler in fall of 1933; analyses made by P. L. Hibbard[a])

Sample No.	Location	Difficulty	Treatment	Result	Zinc in air-dry material	
					Leaves	Twigs
					p.p.m.	*p.p.m.*
1615	Delhi, Calif.	Little-leaf	$MgSO_4$	None	15	5
1621	Delhi, Calif.	Little-leaf	Cu and Zn	Cured by Zn	18	20
1627	Delhi, Calif.	Little-leaf	None	None	12	10
1631	Delhi, Calif.	Little-leaf	Zn	Cured	18	24
1643	Ithaca, New York	None	None	.....	20	32
1687	Gridley, Calif.	None	None	.....	11	11
1689	Gridley, Calif.	Little-leaf, from bad soil in a corral area	Zn	Cured	12	30
1693	Berkeley, Calif.	None	None	.....	43	32
1695	Yuba City, Calif.	None	None	.....	16	14
1701	Davis, Calif.	None	None	.....	11	24
1705	Gridley, Calif.	Corral, little-leaf	None	.....	6	9
1709	Gridley, Calif.	None	None	.....	6	18
1713	Gridley, Calif.	Corral, little-leaf	Zn	Cured	24	50
1711	Berkeley, Calif.	None	None	.....	30	27
1761	College Park, Md.	None	None	.....	15	36
1775	Prosser, Wash.	None	None	.....	10	54
					Zinc in 1 gram of ash[b] from leaves	
.....	Urbana, Ill.	None	None	.....	.17 mg.	
					.16 mg.	
					.20 mg.	
					.20 mg.	
					.20 mg.	
					.17 mg	

[a]Reported by letter to authors April 3, 1934.
[b]Reported by letter to authors August 14, 1934 (sample sent from Illinois).

would probably be more obvious if sprayed trees were compared with unsprayed trees in a region where mottle leaf is common.

During the course of this study a spectroscopic method of analysis was developed, but as the results were not as consistent as those obtained by iodometric titration, they are not included here.

Influence of Zinc Sulfate on Growth of Peach in Nutrient Solutions

The growth of any plant in sand or solution cultures to determine the effect of a given rare element upon its growth is an exceedingly difficult task. Special attention must be given to the type of containers used. Ordinary distilled water contains too many impurities to be used as such. It must be redistilled several times in special equipment. The dust from the air should be excluded, and the

chemicals used in making the nutrient solutions should be recrystallized to insure their purity. If all the above precautions are taken, peach seedlings will not grow at all, even tho a few of the more common rare elements are added. If the "C.P." chemicals used are not recrystallized, but the other precautions are taken, the plants make a fair growth. From studies made in this connection it would appear that there are in "C.P." chemicals several elements present as impurities in sufficiently large quantities to supply the needs of growing plants. Sommers[66*] substantiates this observation in her studies of the influence of zinc on the growth of buckwheat.

It becomes apparent, in view of the foregoing facts, that it is a difficult problem to control the growing conditions of plants with sufficient accuracy to yield significant results. If the chemicals used are purified too highly, the plants will not grow at all and, on the other hand, if they are not highly purified it is impossible to determine whether a given rare element is essential for the growth of the plant in question.

Experimental Methods.—The method employed to determine the influence of zinc on the growth of peach seedlings in sand cultures was as follows:

The nutrient solution used was that suggested by Davidson[12*] as being suitable for research with the peach in sand culture. This solution has an osmotic pressure of one atmosphere, and the following salt proportions: .01055 molar KH_2PO_4, .00438 molar $Ca(NO_3)_2$, .00237 molar $MgSO_4$, and .0014 molar $(NH_4)_2SO_4$. Ferrous sulfate was added according to the needs of the plant.

The plants were grown in glazed pots in purified quartz sand. No attempt was made to purify the air of the greenhouse in which the plants were growing. The KH_2PO_4, the $Ca(NO_3)_2$ and the $FeSO_4.7H_2O$ were found to contain the greatest impurities of zinc and, consequently, were recrystallized twice. The seedlings were crosses of the Elberta variety and should have had a very nearly identical genotype. They were selected on the basis of phenotype when they were six inches tall. The cotyledons were removed and the roots thoroly washed in tap water before transplanting to the purified sand. Nutrient solution made in conductivity water was immediately added, and was replenished according to the needs of the plants. After the plants had become well established they were paired off according to their size and general condition, and the identity of the pairs was maintained thruout the experiment. To the nutrient solution intended for one set of the matched plants were

added 3 p.p.m. of zinc, in the form of $ZnSO_4.7H_2O$, just before the solution was applied to the plants. If zinc in this form is added to the stock nutrient solution, it causes a slight precipitation, as does also the $FeSO_4.7H_2O$. Except for the application of zinc to one set of plants, the two sets of matched plants were treated identically. Checks were run by growing matched plants treated exactly as the other plants but planted in ordinary Carrington silt loam soil. The experiment was discontinued after three months because of the impossibility of preventing the introduction of other variables after that time.

FIG. 2.—EFFECT OF ZINC SULFATE ON GROWTH OF PEACH SEEDLINGS

These plants are growing in purified quartz sand cultures maintained with nutrient solutions exactly alike except that zinc has been added to the solution on the left.

Records were taken at the end of three months on the total plant weight (green) and the pigment content of the leaves. The most reliable method of securing material for pigment analyses was shown by a preliminary study to be on the basis of unit area instead of weight. In the present study one ¾-inch leaf section was cut with a ¾-inch cork borer from each of ten different leaves from each plant. The pigment was extracted with acetone and comparisons were made with a Duboscq colorimeter of the raw solutions to determine the relative

amounts. According to Willstätter and Stoll[75*] the proportions of the color components are sufficiently constant to justify the comparison of raw extracts.

All comparisons in this study were made by using as a standard the extract of the plant to which no zinc had been added. The colorimeter reading for this extract was set at 40, and comparative readings were made accordingly. A high reading, i.e., above 40, denotes a *decrease* in color; a low reading an *increase.*

Experimental Results With Nutrient Solution.—In the experiment described in the preceding paragraphs, zinc applied as zinc sulfate appeared to increase the growth of peach seedlings maintained in

TABLE 7.—EFFECT OF ZINC SULFATE ON GROWTH OF CONTROLLED CROSSES OF ELBERTA PEACH SEEDLINGS MAINTAINED IN PURIFIED QUARTZ SAND BY NUTRIENT SOLUTION

(Cotyledons were removed and plants paired when 6 inches high. Checks were grown in black silt loam soil.)

Pot	Total green weight		Chlorophyl content[a]	
	Zinc added	No zinc added	Zinc added	No zinc added
	grams	*grams*	*colorimeter reading*	*colorimeter reading*
1	43.7	41.1	44	43
2	36.6	30.1	43	42
3	47.2	43.6	42	42
4	53.2	54.0	45	45
5	47.5	47.4	43	43
6	40.1	39.1	45	44
7	48.2	47.8	44	46
8	59.3	58.0	42	44
9	42.0	40.0	46	47
10	48.5	45.3	44	45
Average	46.6	44.6	43.8	44.1
Checks				
1	49.0	51.5	40[b]	40[b]
2	52.2	51.7	39	40
3	48.8	49.0	40	41
Average	50.0	50.7	39.7	40.3

[a]Five readings were made on each chlorophyl analysis and the average computed. One analysis was made from each plant in the study. All plants were matched before the study began, and the identity of the pairs maintained thruout. Roots showed slight browning in the zinc-treated series.
[b]Standard.

purified quartz sand by a nutrient solution, but it had no measurable effect upon pigment production (Table 7). Fig. 2 represents typical growth differences between the two sets of plants. Zinc added to plants growing in a black silt loam soil did not show this beneficial result. It is possible that the complex nature of the soil rendered insoluble the zinc which was added; it is more probable, however, that

the soil already contained enough soluble zinc to meet plant requirements and that, therefore, added zinc had no beneficial effect. The roots of the plants in both sand and soil cultures, to which zinc sulfate had been added, showed a slight browning as compared with the white roots of the untreated plants. This fact leads to the conclusion that the zinc remained soluble in both the sand planting and the soil planting.

Application of soluble zinc to the roots of peach seedlings had little, if any, effect on pigment formation as expressed by acetone extracts.

No definite conclusions as to whether zinc is necessary for the growth of the peach can be drawn from this work. The addition of 3 p.p.m. of zinc to the nutrient solution used increased the growth of the peach, altho there was evident a slight injury to the roots indicated by browning. It would seem, in general, that if zinc is added to a soil which already contains a sufficient amount of this element for satisfactory plant growth, no effect of the added zinc is observable, but that the addition of zinc to a soil deficient in this element results in an increase in growth.

Influence of Zinc Sulfate Spray Mixtures on Peach Growth Under Illinois Field Conditions

The object of this particular study was to determine, if possible, the growth responses of trees under various environmental conditions to zinc sulfate added as an ingredient to spray mixtures. The effects of these various sprays are illustrated in Figs. 3 to 7. The general condition of the absolute checks is illustrated in Fig. 8. All these pictures were taken in the latter part of August about two weeks after harvest.

During the growing seasons of 1932, 1933, and 1934, thousands of leaves were measured according to the "leaf product" method suggested by Darrow,[11*] by which the length and breadth of the leaves are multiplied to get an index to the leaf area.* The details and results of the experiment, including observations on spray injury and percent of infection by *P. pruni,* are listed in Table 8.

Each of the spray mixtures applied reduced slightly, in all cases except one (which was probably not significant), the leaf area of the

*This "leaf product" method is not quite so accurate as the planimeter method but is nearly three times as fast. The error is shown by Darrow to be less than 1 percent, which is only slightly greater than in the more accurate planimeter method.

FIG. 3.—DEFOLIATION RESULTING FROM LEAD ARSENATE-LIME SPRAYS

Four applications of a lead-lime spray (3-6-100) had been made to this peach tree. The severity of defoliation from lead-lime sprays varies considerably from season to season.

FIG. 4.—DEFOLIATION CAUSED BY LEAD ARSENATE ALONE

This tree had received four applications of spray containing only lead arsenate, 3 pounds in 100 gallons of spray.

TABLE 8.—EFFECT OF SPRAYS ON LEAF SIZE AND INJURY

Treatment[a]	Number of sprays	Number of leaf examinations	Average leaf dimensions			Injury			Location	Variety	Year
			Width	Length	Leaf product	Leaf fall	Bacterial spot	Spray			
			inches	*inches*	*index*	*perct.*	*perct.*	*perct.*			
Checks (no sprays or dusts)..	0	2 041	1.46	5.58	8.15	5.8	8	.9	Carbondale	Hale	1932
	0	939	1.21	3.87	4.68	7.9	25	Trace	Irvington	Elberta	1933
	0	801	1.34	4.61	6.16	4.9	5	0	Olney	Gage	1933
	0	908	1.31	4.63	6.07	6.1	8	0	Olney	Elberta	1933
	0	504	1.46	5.71	8.33	5.2	0	0	Urbana	Elberta	1934
Lead-lime, 4-8-100.....	4	1 997	1.45	5.49	7.96	32.4	19	29.6	Carbondale	Hale	1932
3-6-100.....	5	986	1.15	3.70	4.26	28.	16	22	Irvington	Elberta	1933
3-6-100.....	5	914	1.31	4.58	6.00	19.8	4	7	Olney	Gage	1933
3-6-100.....	5	901	1.31	4.61	6.04	22.1	4	4	Olney	Elberta	1933
3-6-100.....	5	500	1.39	5.60	7.78	31.3	0	21	Urbana	Elberta	1934
Zinc-lime, 8-8-100.....	6	2 012	1.46	5.50	8.04	12.4	11	9	Carbondale	Hale	1932
Lead, 4-100.....	4										
Zinc-lead-lime, 8-3-8-100....	5	943	1.17	3.90	4.58	8.9	21	4	Irvington	Elberta	1933
8-3-8-100....	5	929	1.33	4.62	6.15	8.1	4	2	Olney	Gage	1933
8-3-8-100....	5	898	1.32	4.61	6.09	9.8	10	.8	Olney	Elberta	1933
8-3-8-100....	5	500	1.44	5.69	8.19	9.	0	6	Urbana	Elberta	1934
Zinc-lime, 8-8-100.....	6	2 106	1.47	5.47	8.09	5.7	9	0	Carbondale	Elberta	1932
	5	859	1.20	3.87	4.64	8.8	22	Trace	Irvington	Elberta	1933

[a]For spray schedules see pages 254-255, Appendix. Formulas indicate pounds of material in 100 gallons of water.

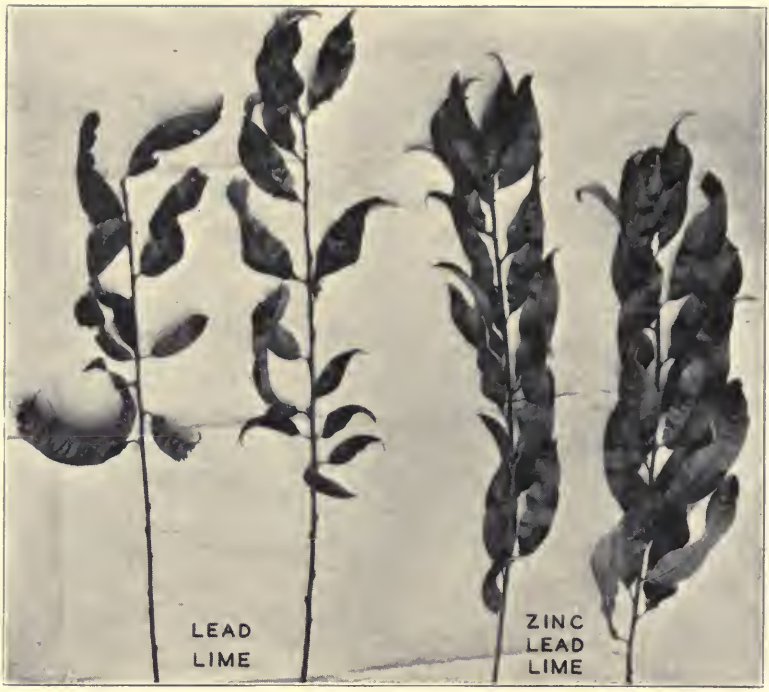

FIG. 5.—ZINC SULFATE AS A CORRECTIVE OF TWIG DEFOLIATION RESULTING FROM LEAD ARSENATE - LIME SPRAYS

The peach tree from which the two twigs at the left were taken had been sprayed with lead arsenate - lime mixtures. This type of injury was corrected by adding zinc sufate to the spray mixture, as indicated by the two twigs at the right taken from trees sprayed with zinc-lead-lime.

trees receiving them. Zinc sulfate - lime spray caused least reduction in leaf area and no injury. Lead arsenate - lime gave greatest area reduction and injury, much greater than when zinc sulfate was added as an ingredient. In fact the injury usually caused by lead-lime sprays was practically eliminated by the addition of zinc sulfate.

As a second part of this study of growth responses to zinc sulfate in spray mixtures, pigment analyses were made by acetone extracts as described on page 227, to ascertain the effect of sprays containing zinc sulfate on chlorophyl production in peach leaves. The pigment extracts were made from Elberta peaches which had received five sprays during the 1934 growing season. Five readings were made of each analysis. Fifty ¾-inch leaf sections were used in each extraction instead of ten, as used in the previous experiment (page 227).

FIG. 6.—CONTROL OF ARSENICAL INJURY TO FRUIT BY USE OF ZINC SULFATE

The peach shown at the lower left was taken from a tree that had received no sprays or dusts. The other two peaches in this vertical row are examples of the most severe fruit injury to be found on trees sprayed with zinc-lead-lime mixtures. In the row at the right are three examples of the severe cracking that is typical of the injury from lead arsenate - lime sprays. Zinc sulfate added to the lead-lime sprays corrects this arsenical injury.

FIG. 7.—PEACH TREE AFTER FIVE APPLICATIONS OF ZINC-LEAD-LIME 8-3-8-100

Note the heavy foliage, especially on the lower branches. The value of zinc sulfate as a corrective of defoliation resulting from arsenical injury is evident from a comparison of this tree with the trees shown in Figs. 3 and 4.

FIG. 8.—CHECK TREE, NO SPRAYS OR DUSTS APPLIED DURING THE GROWING SEASON

The check trees always *look* best. The tree shown in Fig. 7, however, sprayed with zinc sulfate, lead arsenate, and lime, closely approaches the check tree in appearance of foliage.

In order to determine which differences were significant, an extraction from the nonsprayed (check) trees was compared with itself and the findings were recorded. As a check on the accuracy of color comparisons, the colorimeter readings taken by two observers are listed (Table 9).

TABLE 9.—PIGMENT CONTENT OF PEACH LEAVES SPRAYED WITH ZINC-LEAD-LIME AND LEAD-LIME

(Colorimeter readings; nonsprayed trees set at 40)

Reading No.	Zinc-lead-lime[a]		Lead-lime[a]	
	Reader 1[b]	Reader 2[b]	Reader 1	Reader 2
1	40	39	45.5[c]	44[c]
2	41[c]	41[c]	45	45
3	41.5	40	45.5	44
4	41	38.5	45.5	43.5
5	40.5	39	45.5	44.5
6	39	39.5	43.5	42.5
7	40	40	43	43
8	38.5	40	42.5	43.5
9	38	38.5	42.5	43.5
10	39	39.5	44	42.5
11	39.5	41	43	43.5
12	39.5	39.5	44	43.5
13	41	40.5	43.5	43
14	38.5	41.5	43	43
15	38.5	40	44	43
16	40	41	46	47
17	40	39.5	45	46
18	38.5	40	45	46
19	40.5	41	45	45.5
20	39	41	45	47.5
21	41	40.5	44	45
22	41.5	40	43	45.5
23	41	41	44	46
24	40.5	40	45	46
25	40.5	41.5	44.5	45.5
Average	39.8	40.1	44.2	44.5

[a]Five applications during the 1934 season in the following proportions: zinc sulfate, 8 pounds; lead arsenate, 3 pounds; lime, 8 pounds; water, 100 gallons. The same proportions of lead arsenate and lime were used in the lead-lime sprays.

[b]Accuracy of replicate colorimeter readings of a given sample as observed by the two readers (10 readings each) were as follows, the standard reading being set at 40:

Reader 1: 40.5, 39.5, 38.5, 39.5, 39, 41, 41.5, 41, 41.5, 40, Av. 40.2.

Reader 2: 42.5, 41.5, 41, 40.5, 40, 40.5, 39.5, 40, 39.5, 40, Av. 40.5.

[c]Colorimeter readings above 40 indicate a *reduction* in pigment formation; i.e., a lighter color.

According to the results listed in Table 9, the zinc sulfate - lead arsenate - lime spray mixture reduced slightly and lead arsenate - lime sprays reduced materially pigment production per unit area of leaf surface. The pigment reduction resulting from lead-lime sprays can be seen in field experimental plots in some seasons, but no difference in leaf color between trees receiving zinc-lead-lime or zinc-lime and those receiving no sprays has ever been noticeable in these tests.

All these experiments and observations point to the fact that there is no increase in leaf size or pigment content when zinc sulfate is

added to the spray material, but that there is a decrease in leaf size and pigment content when lead-lime sprays not containing zinc sulfate are applied.

Conclusions Regarding Effect of Zinc on Growth of Peach

Chemical analyses here presented show that the ash from normal peach tissue always contains zinc. This seems to be true of all normal plant and animal tissue thus far analyzed for zinc. Zinc sulfate applied to peach leaves with lime or with lead and lime apparently effected a slight penetration of the leaf.

Three parts per million of zinc added to a nutrient solution and applied to peach seedlings in purified quartz sand increased the green weight of the trees growing therein. To what extent zinc is necessary to peach growth has not as yet been determined. The addition of zinc sulfate to sprays containing lead arsenate and lime greatly decreased, under field conditions, the amount of leaf area reduction caused by lead-lime sprays and practically eliminated the injurious effects of lead-lime sprays on pigment formation. Zinc sulfate - lime without lead causes no noticeable injury when applied to the peach. It has no measurable effect on pigment formation and only slightly reduces total leaf area. Falkenberg[15*] reports that its general effect on growth is about the same as that of lime alone.

The pigment reduction resulting from lead-lime sprays can be seen in the field in some seasons, but no difference in leaf color between trees receiving zinc-lime or zinc-lead-lime and those not sprayed at all has ever been observed in the experiments herein reported. Zinc-lead-lime sprays *did not increase pigment formation.* The opinion commonly expressed by growers that trees so treated are deeper green than those receiving lead arsenate - lime is justified, *but the effect observed is the result of a decrease in the pigment content of the lead-lime sprayed trees* rather than an increase of pigment resulting from the addition of zinc sulfate to the spray mixture. Thruout three years' experimentation, under various soil and environmental conditions, the trees that *looked* the best were always the checks, which had received no sprays or dusts, altho there was usually very little difference *in appearance* between them and the trees sprayed with mixtures containing zinc sulfate as a constituent. If peach trees are growing in a soil deficient in soluble zinc, sprays applied with zinc sulfate as an ingredient would probably result in stimulation.

ZINC SULFATE AS A CORRECTIVE FOR PEACH SPRAY INJURY

Acid lead arsenate is undoubtedly the most satisfactory and most generally used insecticide on the market for the control of peach insects, and yet its use often leads to serious losses to growers thru severe injury to trees and fruit. Under Illinois conditions various degrees of spray injury occur yearly when applications of lead arsenate - lime sprays are made. The most common types of injury are leaf burning and defoliation. If, however, environmental conditions favor spray injury, severe bud killing, twig cankers, and burning and cracking of fruit may result. Actual killing of twigs and branches has been observed, and it is not at all uncommon for injury from lead-lime sprays to so stunt a tree that its usefulness is permanently impaired. Figs. 3 to 7 illustrate the type of lead arsenate spray injury commonly present on the peach in Illinois.

These losses from lead arsenate spray injury have been pointed out by numerous investigators, and causes and possible remedies have been suggested and investigated. The use of zinc sulfate as a corrective has not been entirely overlooked, but apparently its possibilities have not been heretofore adequately recognized.

Review of Literature Pertaining to Spray Injury

Few investigators realized the seriousness of arsenical injury until the work of Haenseler and Martin[24*] was published in 1925. That losses to growers from lead arsenate spray injury may, under certain Illinois conditions, often be much greater than from the insects and diseases for which the spray was applied, was pointed out[2*] in 1931. Kilgor,[31*] Clinton and Britton,[10*] Sanders,[62*] Swingle,[71*] and other workers have definitely demonstrated that water-soluble arsenic formed during or after the application of lead arsenate to plants is largely responsible for this injury.

Acid lead arsenate, properly manufactured, is only slightly soluble in distilled water, but distilled water is not used by the orchardist in making up spray mixtures. Haywood and McDonnell,[25*] Stewart,[69*] de Ong,[45*] and Mogendorff[42*] have shown that the nature of the water used greatly influences the amount of soluble arsenic formed.

Many workers have studied the relation of meteorological conditions to spray injury. In general, they have concluded that high humidity and high temperature are most conducive to spray injury. Ginsburg[18*] studied the influence of sunlight, humidity, and temperature on the liberation of water-soluble arsenic, and concluded that

within rather wide limits they were of little practical importance, either singly or combined. He suggested, however, that meteorological conditions may affect injury: "High humidity, intense sunlight and high temperature may increase arsenical burning on foliage indirectly by affecting the permeability and absorbing power of the plant tissue for water-soluble arsenic."

Robinson,[61*] Campbell,[7*] Patten and O'Meara,[46*] Mogendorff,[42*] and Ginsburg[18, 19*] found that carbon dioxid may greatly increase the liberation of water-soluble arsenic. The effects of certain fungicides on soluble arsenic have also been studied. It is an established fact that under certain conditions chlorids, sulfates, carbonates, bicarbonates, and hard or alkaline waters in general increase the solubility of various arsenates.

Until rather recently it was believed that additions of high calcium spray lime to acid lead arsenate would prevent arsenical spray injury. It is true that in practice $Ca(OH)_2$ added to $PbHAsO_4$ usually reduces materially the amount of spray injury, but this reduction is all too often entirely inadequate for satisfactory protection. Campbell[7*] pointed out in 1925 that authentic instances of severe arsenical injury had resulted from application of lead arsenate - lime sprays in New Jersey. He contended that the following reactions took place and are responsible for the increase in soluble arsenic.

"1—In the spray tank and on foliage while there is an excess of calcium hydroxide; $5PbHAsO_4 + 3\ Ca(OH)_2 \rightarrow Pb_4(PbOH)(AsO_4)_3 + Ca_3(AsO_4)_2 + 5\ H_2O$

"2—On foliage; $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

"3—On foliage; $Ca_3(AsO_4)_2 + CO_2 + H_2O \rightarrow 2\ CaHAsO_4 + CaCO_3$."

Campbell's interpretation of the above reactions is as follows:

"The usual protective effect on foliage of calcium hydroxide in acid lead arsenate combination sprays may lie in the fact that soluble calcium arsenate from such sprays is less toxic to foliage than soluble arsenic from sprays of acid lead arsenate alone. Apparently under warm and humid conditions, however, such as often occur in New Jersey, acid calcium arsenate (equation 3) may become present on foliage sprayed with $Ca(OH)_2 + PbHAsO_4$, in high enough concentration and over a sufficient period of time to cause severe foliage injury."

Mogendorff[42*] deduced from his studies on the reaction of lead arsenate - lime spray mixtures that:

"When lead arsenate spray is combined with hydrated or freshly slaked lime, it will be decomposed and converted into basic lead arsenate and very insoluble basic calcium arsenate. The latter compound will be decomposed by the action of carbon dioxide, chiefly supplied by the respiratory process of the plant. The basic calcium arsenate will be transformed to

less basic compounds and then to tri-calcium arsenate which is very likely soluble enough to cause injury. It is not probable that di- or mono-calcium arsenate is formed as a rule."

According to Ginsburg,[18*] "the $PbHAsO_4$ is directly acted upon when the hydrated lime absorbs CO_2 and is converted into $CaCO_3$ which may result in the formation of soluble calcium acid arsenate."

Altho these investigators are not entirely agreed as to the chemistry involved in the increase of water-soluble arsenic, they all contend that carbon dioxid is responsible for its liberation. Goodwin and Martin[21*] agree in general with Campbell and Mogendorff.

The chief sources of CO_2 are the air, the respiration of the plant, and the waters used to make up the spray mixtures. Hundreds of analyses by the Illinois State Water Survey[23*] show a tremendous variability in the chemical and physical nature of Illinois waters. That respiratory products liberated by the plant may seriously affect the solubility of lead arsenate has been demonstrated by Smith.[65*]

Roberts and Pierce[56*] recognized that the addition of zinc sulfate to sprays containing lead arsenate seemed to reduce the amount of injury, but, judging from their various reports, they overlooked its true capacity in this connection. Both Anderson[2*] and Hurt[27,28*] also recognized that additions of zinc sulfate to lead arsenate - lime sprays gave exceedingly beneficial results, altho they made no attempt to show what caused these results. Poole[47*] reported that the "corrective effect" of zinc sulfate in lead arsenate - lime sprays lasts only a short time, but the results of experimentation on this problem under Illinois environmental conditions are to the contrary.

The data which follow clearly show that zinc sulfate practically eliminates water-soluble arsenic in lead arsenate spray combinations.

Field Studies of Zinc Sulfate as a Corrective

The spray-injury studies were made in the experimental plots at Carbondale, Irvington, Olney, and Urbana, Illinois. The first three of these orchards have been described earlier in this bulletin. The Urbana plots consisted of Elberta variety on Carrington silt loam soil. The trees had always been well kept and were in good general vigor. They seldom bear fruit because the buds are usually killed by cold winters or late spring frosts. In general the Carbondale, Urbana, and Olney orchards were high in vigor, and the Irvington orchard was rather low, altho good cultural practices had been followed in all of them.

The spray schedules applied are given an pages 254 and 255. In

order to accentuate arsenical injury and the differences between treatments, 4 pounds of $PbHAsO_4$ in 100 gallons of water were used in the plots at Carbondale, but only the 3 pounds recommended for the control of peach insects in this state were used in the other orchards. Results of these experiments are given in Tables 1, 8, 10, and 11.

Many other observations have been made in this state with reference to zinc sulfate as a corrective for spray injury, and without an exception they corroborate the data presented in the above tables. It is significant that Goodwin and Martin[21*] found a bordeaux mixture

TABLE 10.—LEAF FALL OF PEACHES ON EXPERIMENTAL PLOTS AT CARBONDALE, ILLINOIS, JULY 22, 1932[a]

Plot	Treatment[b]	Average length shoot	Leaves dropped	Leaves injured and still attached	Leaves per shoot, average
		inches	*perct.*	*perct.*	*number*
1.....	Zinc-lime-lead 8-8-4-100.....	7.9	6.8	4.7	16.3
2.....	Zinc-lime-lead 4-4-4-100.....	8.1	4.6	2.7	19.7
3.....	Zinc-lime-lead 4-8-4-100.....	8.6	5.3	6.0	16.8
4.....	Zinc-lime-lead 2-4-4-100.....	10.0	6.1	8.0	19.2
5.....	Zinc-lime-lead 1-4-4-100.....	7.0	3.9	7.2	18.8
6.....	Lime-lead 16-4-100.....	7.1	22.1	25.5	18.5
7.....	Lime-lead 8-4-100.....	8.5	37.6	24.0	21.0
8.....	Lime-lead 4-4-100.....	7.4	34.6	33.9	17.6
9.....	Lime-lead 16-4-100.....	8.1	26.5	15.7	22.1
10....	Zinc-lime 8-8-100.....	7.5	5.5	0	15.1
11....	Flotation sulfur-lime-lead 12-6-3-100	8.3	18.2	19.8	19.9
13....	Zinc-lime-lead 8-8-4-100.....	7.8	14.3	17.7	17.8
14....	Zinc-lime-lead 4-4-4-100.....	7.2	15.6	27.2	15.9
15....	Zinc-lime-lead 4-8-4-100.....	8.2	10.0	22.7	17.1
16....	Zinc-lime-lead 2-4-4-100.....	8.4	16.2	37.3	17.2
17....	Lead 4-100.....	8.5	35.8	49.4	17.2
18....	Lime-lead 8-4-100.....	8.6	27.3	29.5	19.8
19....	Zinc-lime 8-8-100.....	8.8	4.6	3.0	20.6
C1...	Absolute check.....	7.6	5.5	3.1	19.1
C2...	Zinc-lime-lead 8-8-3-100.....	6.9	7.3	6.5	16.1
17a...	Absolute check.....	7.7	4.7	.6	17.6
20....	Lime 12-100 (2 sprays only).....	8.3	5.2	2.7	13.5

[a]Orchard in very good condition. Bacterial spot not uniform over all plots.
[b]Sprayed according to Schedule No. 1 (page 254). Arsenate of lead 4-100 used to accentuate spray injury. Plots 1 to 11 were on very uniform ground; plots 13 to 18 were on rather hilly ground.

"far more efficient as a corrective than hydrated lime." Probably similar chemical reactions are involved in the reduction of water-soluble arsenic by copper sulfate - lime and zinc sulfate - lime.

Ginsburg[20*] found that zinc oxid, altho it had the effect of greatly reducing water-soluble arsenic, nevertheless caused serious injury when applied with lead arsenate to fruit trees. He demonstrated that the injury was due largely to zinc oxid. Zinc oxid might, however,

TABLE 11.—CONDITION OF PEACH LEAVES IN SPRAY INJURY STUDIES, IN VARIOUS ILLINOIS PEACH ORCHARDS, 1932, 1933, AND 1934

Treatment[a]	Number of leaves examined	Leaves fallen	Spray injury, leaves still attached	Bacterial spot, infected leaves	Variety	Location	Date
		perct.	*perct.*	*perct.*			
Checks, no sprays or dusts	2 041	5.8	.9	8	Hale	Carbondale	1932
	2 517	6.7	0	8	Elberta	Olney	1933
	2 404	6.7	0	5	Gage	Olney	1933
	2 817	9.5	Trace	27	Elberta	Irvington	1933
	1 389	5.2	0	0	Elberta	Urbana	1934
Lead-lime 4-8-100	1 997	32.4	29.6	19	Hale	Carbondale	1932
3-6-100	2 508	21.8	3.6	4	Elberta	Olney	1933
3-6-100	2 638	18.0	6.3	3	Gage	Olney	1933
3-6-100	2 832	28.0	17.6	14	Elberta	Irvington	1933
3-6-100	1 489	31.3	21.0	0	Elberta	Urbana	1934
Zinc-lime 8-8-100 / Lead 4-100	2 012	12.4	9.0	11	Hale	Carbondale	1932
Zinc-lead-lime 8-3-8-100	2 361	9.8	9.3	.4	Elberta	Olney	1933
8-3-8-100	2 461	8.0	2.0	4	Gage	Olney	1933
8-3-8-100	2 938	8.8	3.9	23	Elberta	Irvington	1933
8-3-8-100	1 352	9.0	6.3	0	Elberta	Urbana	1934
Zinc-lime 8-8-100	2 106	5.7	0	9	Elberta	Carbondale	1932
8-8-100	2 848	8.0	Trace	19	Elberta	Irvington	1933

[a]For spray schedules see pages 254-255, Appendix. Formulas indicate pounds of material in 100 gallons of water.

have had the same corrective effect possessed by mixtures of zinc-lime-lead if it had been used with lime and lead arsenate instead of with lead arsenate alone.

The correct amount of zinc sulfate necessary to give under all conditions complete protection has not as yet been accurately determined. From Table 10 it may be seen that much less than the 8 pounds per 100 gallons now recommended for use in Illinois will control arsenical injury in a vigorous, well-kept orchard. Comparison of Plots 3 and 4 in Table 1, however, shows quite clearly that under conditions especially favorable for arsenical injury 8 pounds is not greatly excessive. Six pounds of zinc sulfate, it is believed, will eliminate, in practically all situations, the arsenical injury caused from 3 pounds of acid lead arsenate. *The actual recommendation would be, therefore, 6 pounds of zinc sulfate* ($ZnSO_4.7H_2O$), *6 pounds of high-grade hydrated lime, and 3 pounds of acid lead arsenate to every 100 gallons of water.* Zinc sulfate or lead arsenate applied separately or in combination to trees causes injury under field conditions, altho a mixture of zinc sulfate and lead arsenate actually decreases water-soluble arsenic in laboratory tests.

Laboratory Studies of Zinc Sulfate as a Corrective

In an attempt to evaluate the "corrective effect" of zinc sulfate on arsenical spray injury, so obvious in field experiments, the influence of zinc sulfate on the liberation of water-soluble arsenic was studied in the laboratory under two conditions: (1) when the materials were held in suspension, and (2) when the materials were allowed to dry on glass plates. The latter was a closer approximation of actual field conditions.

In each study two series were run—one with distilled water and another with pond water from Irvington, Illinois. The pond water was the same as that used in the spraying experiments at Irvington.*

All chemicals used were "C.P." except the $PbHAsO_4$, which was the regular commercial Sherwin-Williams product. Arsenic determinations were made by the Gutzeit method[64]* and are expressed as the percentage of water-soluble As_2O_5 present in the $PbHAsO_4$ used.

In all tests the materials were used at ratios in keeping with commercial recommendations; i.e., 3 grams of $PbHAsO_4$ were used thruout in 800 cc. of water, which corresponds to the 3 pounds in 100 gallons generally recommended. The figures expressing the percentage of soluble arsenic are averages of the results of replicate tests.

*See analysis, page 253, Appendix.

Tests With Materials in Suspension.—The materials were weighed, mixed with water, placed in closed containers on a shaking machine, and analyzed after various periods of shaking at a constant rate. The purpose of the experiment was to ascertain the amount of water-soluble arsenic actually formed in the spray tank and applied to the trees. The results, listed in Table 12, agree, in general, with the findings of previous workers.

TABLE 12.—WATER-SOLUBLE ARSENIC IN SPRAY MIXTURES

Chemical mixtures[a]	Number of replications	Held in suspension	Exposure to air on glass plates	Water-soluble As_2O_5 based on $PbHAsO_4$	
				Distilled water	Pond water
			days	*perct.*	*perct.*
$PbHAsO_4$..... 3 lbs. $Ca(OH)_2$..... 6 lbs. Water.....100 gals.	8	30 min.	..	.13	.12
	5	1½ hrs.	..	.15	.13
	5	24 hrs.	..	.018	Trace
	4	.....	10	.64	.68
$PbHAsO_4$..... 3 lbs. Water.....100 gals.	8	30 min.	..	.27	.24
	5	1½ hrs.	..	.28	.26
	2	24 hrs.	..	.28	.27
	4	.....	10	.52	.53
$PbHAsO_4$..... 3 lbs. $ZnSO_4.7H_2O$..... 8 lbs. $Ca(OH)_2$..... 8 lbs. Water.....100 gals.	8	30 min.	..	.12	.12
	5	1½ hrs.	..	.15	.13
	2	24 hrs.	..	.024	.031
	4	.....	10	Trace	Trace
$PbHAsO_4$..... 3 lbs. $ZnSO_4.7H_2O$..... 8 lbs. Water.....100 gals.	8	30 min.	..	.093	.087
	5	1½ hrs.	..	.099	.087
	2	24 hrs.	..	.093	.087
	4	.....	10	.019	.024
$PbHAsO_4$..... 3 lbs. $CaCO_3$..... 8 lbs. Water.....100 gals.	8	30 min.	..	1.54	1.66
	5	1½ hrs.	..	1.58	1.71
	2	24 hrs.	..	1.65	1.76
	4	.....	10	1.36	1.30
$PbHAsO_4$..... 3 lbs. $CaCO_3$..... 8 lbs. $ZnSO_4.7H_2O$..... 8 lbs. Water.....100 gals.	8	30 min.	..	.058	....
	5	1½ hrs.	..	.058	....
	2	24 hrs.	..	.05	....
	4	.....	10	.019	.02

[a]Mixtures were made in 800 cc. of water and in accordance with the ratios listed. These are the proportions recommended for peach spraying in Illinois. An analysis of the pond water used is given on page 253.

Experiments With Mixtures Dried on Glass Plates.—The chemicals were weighed, mixed with water, and placed on the shaker for 30 minutes. A 50-cc. sample was then taken from each suspension and spread in a thin film over a glass plate. The plates were allowed to dry at 80° F. After they were completely dry they were held during the day at 88-92° F. and during the night at the temperature of the laboratory which was approximately 68-72° F. Each evening the dry

mixtures were sprayed lightly with distilled water in an attempt to duplicate the dews common in Illinois. After ten days the material was carefully washed off the plates and filtered. The filtrate was analyzed for water-soluble arsenic.

The salts and CO_2 liberated by the plants and demonstrated by Smith[65*] to actually increase water-soluble arsenic were not considered in these tests. It is very likely, therefore, that the amounts of water-soluble arsenic found in these experiments were lower than amounts actually produced on leaves in the field. Results are listed in Table 12.

Lime Carbonation Experiments.—It is a well-established fact, as already stated (page 239), that the introduction of carbon dioxid into the chemical system of lead arsenate - lime is responsible for large increases of water-soluble arsenic. Investigators are not agreed upon the chemistry of this increase. But whatever it may be, it is significant to note from Table 12 that the introduction of zinc sulfate into an acid lead arsenate - lime mixture reduced materially the amount of water-soluble arsenic formed, especially when the mixtures were exposed to weathering influences.

Under field conditions it would seem that an important source of CO_2 would be the plant itself, altho definite proof of this appears to be lacking. Tilford[72*] found that $Ca(OH)_2$ applied as a dust to potato leaves when they were dry was completely carbonated after 24 hours. He did not, however, find how rapidly lime carbonated under identical conditions independent of the plant. Streeter *et al*[70*] have studied the carbonation of lime in thin films on paper covered trays, and have concluded that "the conversion of calcium hydroxide to calcium carbonate may take place in a few hours or it may take several days, depending on the temperature and relative humidity of the air."

Since the chief source of CO_2 is still in question, it seemed important to determine, if possible, the difference in the rate of absorption of CO_2 by various chemical systems on the leaves of sprayed plants and on glass plates in the laboratory. The most reliable approach to this problem appeared to be a direct measuring of the CO_2 taken up. Spray mixtures were again made up according to commercial recommendations, applied in known quantities as thin films to glass plates and sprayed on peach trees at 300 pounds pressure. In order to imitate the heavy dews common under field conditions, the mixtures on the glass plates were sprayed lightly each evening with boiled distilled water from an atomizer. In Fig. 9 is shown the graphic record of temperature and humidity, both of which were quite high, during the course of this study.

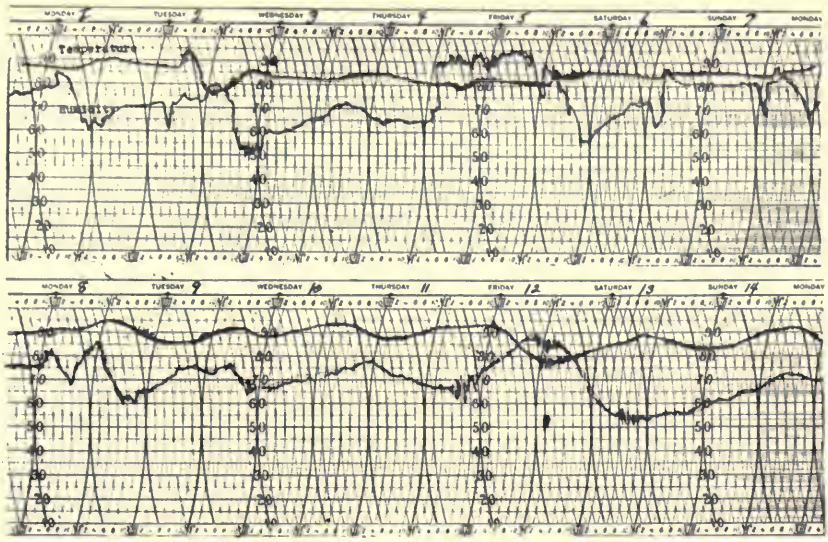

FIG. 9.—PHOTOGRAPHIC RECORD OF TEMPERATURE AND HUMIDITY DURING LIME CARBONATION STUDIES.

As a convenient measure, carbonation was figured on the basis of the original amount of $Ca(OH)_2$ in the spray mixture. In order to determine the amount of $Ca(OH)_2$ involved in the analyses from sprayed trees, the CO_2 was liberated with HCl and weighed. The amount of calcium present was then determined by precipitation as calcium oxalate and subsequent titration by means of a decinormal potassium permanganate solution.

The results of this study, listed in Table 13, indicate that the air was the chief source of CO_2 absorbed by lime. It is evident, also, that CO_2 liberated by peach trees is another source. The rate and amount of carbonation, however, are probably influenced more by temperature and humidity than by any other factors. At least part of the corrective effect of zinc sulfate appears to lie in its power to prevent rapid carbonation of lime.

Conclusions Regarding Effects of Zinc Sulfate on Spray Injury

Lead arsenate - lime sprays without zinc sulfate are absolutely unsafe for peaches under Illinois conditions. Zinc sulfate - lime alone does not cause noticeable injury, nor does zinc sulfate - lead arsenate - lime, except some occasional leaf injury and a slight reduction in leaf

TABLE 13.—RATE OF ASSIMILATION OF CO_2 BY VARIOUS SPRAY MIXTURES

Time, in days	Percentage carbonation of lime in—		
	Lime	Lead-lime	Zinc-lead-lime
Laboratory series: thin films on glass plates			
At start	13	13	13
2	25	25	13
4	56	38	16
5	78.6	58	18
6	100	80	21
7	....	100	23
8	....	....	28
9	....	....	28
10	....	....	29
11	....	....	28
12	....	....	31
Field series: analyzed directly from sprayed leaves			
At start	13	13	13
2	63	55	17
4	95	98	25
5	100	100	24
6	....	....	26
7	....	....	23
8	....	....	32
9	....	....	32
10	....	....	33
11	....	....	32
12	....	....	34

area (see pages 229-232) undoubtedly due to the acid lead arsenate or products formed from it.

Evidently in the lead-lime sprays the lime carbonates very rapidly, forming $CaCO_3$, which causes large increases in water-soluble arsenic, which in turn may cause severe leaf injury and defoliation, bud killing, twig cankers, and often, indirectly, the actual killing of the tree itself.

In the carbonation of the lime of lead-lime sprays, the air, altho supplemented to some extent by CO_2 liberated directly from the leaves, is evidently the chief source of the CO_2 required. High temperature and high humidity, as shown by other workers, greatly influence the rate of carbonation of lime. It is evident from research herein reported that at least part of the "beneficial effect" of zinc sulfate as an ingredient in lead arsenate - lime sprays lies in its power to prevent rapid carbonation of lime, which in turn prevents increased liberation of injurious arsenic acid. It is evident also that zinc sulfate practically eliminates arsenic acid formed from a mixture of acid lead arsenate and calcium carbonate with no calcium hydroxid present. In the event that arsenic acid is formed from either lead arsenate or calcium

arsenate from the mixture of $PbHAsO_4$ and $Ca(OH)_2$, it is probably immediately precipitated as an insoluble zinc arsenate.

Thus field data collected over a period of three years and laboratory tests indicate that the addition of zinc sulfate to lead arsenate - lime sprays practically eliminates the arsenical injury usually resulting from applications of lead arsenate - lime alone. The amount of zinc sulfate required, according to research thus far complete, appears to be 6 pounds with 6 pounds of hydrated lime and 3 pounds of acid lead arsenate in every 100 gallons of water.

SUMMARY AND GENERAL CONCLUSIONS

The experiments reported in this paper were made in order to determine the effects of zinc sulfate applied to the peach as a spray ingredient or as a constituent of a nutrient solution. Data have been presented showing the role of zinc sulfate as a fungicide, as a bactericide, and as a corrective of lead arsenate spray injury to the peach, together with its effect upon peach growth.

Zinc sulfate is at best a very weak fungicide and cannot be relied upon to control severe outbreaks of peach scab or brown rot. Sulfur is much more effective. In the control of peach scab, zinc sulfate - lime sprays, with or without lead arsenate, were no more effective than lead arsenate - lime under Illinois field conditions. Judging from the results of laboratory tests, zinc sulfate - lime was likewise no more effective than lead arsenate - lime in the control of brown rot. If spray applications are to be made primarily for the control of peach scab or brown rot, there seems to be little justification for the use of zinc sulfate.

Nor is zinc sulfate a good bactericide. Field and laboratory data herein recorded indicate in general that however used it is of no practical value if applied specifically for the control of *Phytomonas pruni*.

Analyses made at the Universities of California and Illinois indicate that zinc is always present in the ash of normal peach tissue. Its exact function in regard to the growth of the peach is, however, not at present completely understood. Applied as a nutrient solution to peach seedlings growing in purified quartz sand, zinc sulfate increased the growth measurably. Applied to seedlings growing in Carrington silt loam soil, it had practically no effect. It is quite probable that its addition to soil deficient in soluble zinc would result in stimulation of growth, as reported by other workers.

Neither as a constituent of a nutrient solution, nor as a spray ingredient did zinc sulfate have any measurable effect on pigment

formation. The marked decrease in pigment content of lead-lime sprayed trees, rather than an increase of pigment resulting from the addition of zinc sulfate to the spray mixture, is responsible for the opinion common among growers that zinc sulfate - lime sprayed trees are a deeper green than unsprayed trees. Growers seldom compare zinc sulfate - lime sprayed trees with absolute checks, but rather with trees sprayed with lead-lime, which accounts for the mistaken opinion. Zinc sulfate added to a lead-lime mixture does not increase pigment formation; it counteracts the tendency of the lead arsenate to decrease pigment content.

Applied as a spray ingredient under Illinois field conditions, zinc sulfate not only did not cause any noticeable injury, altho by actual measurement, it did reduce the leaf area slightly, but had the beneficial effect when applied with lead arsenate - lime of practically eliminating the injury commonly resulting from the use of lead arsenate - lime alone.

Lead arsenate spray injury comes about largely as a result of the formation of water-soluble arsenic. Lime alone added to lead arsenate sprays fails to correct this arsenical injury because it rapidly carbonates and thereafter actually facilitates the formation of water-soluble arsenic. The chief source of the CO_2 necessary for the carbonation of lime in lead arsenate - lime spray is the air. The conversion of $Ca(OH)_2$ to $CaCO_3$ may be completed in periods varying from a few hours to a week or ten days after application, the length of time depending, as other workers have shown, upon temperature and humidity. When sufficient moisture is present to allow the chemical reaction, $CaCO_3$, in the presence of lead arsenate, greatly increases water-soluble arsenic. This carbonation of lime and the resulting formation of water-soluble arsenic explain the frequent occurrence of severe lead arsenate spray injury to the peach under Illinois growing conditions. *An effective control of arsenical injury caused by lead arsenate - lime sprays is the use of zinc sulfate in the mixture.*

The virtue of zinc sulfate in eliminating arsenical spray injury lies in its power to prevent the rapid carbonation of lime and, probably, in its precipitation of an *insoluble* zinc arsenate whenever arsenic acid is formed.

The formula for the peach spray mixture containing zinc sulfate as an ingredient, based upon three years of experimentation and recommended to Illinois peach growers, is *6 pounds of zinc sulfate, 6 pounds of hydrated lime, and 3 pounds of acid lead arsenate to 100 gallons of water.*

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APPENDIX

BOILER WATER ANALYSIS

(C.W.A.)

Sample of water collected February 19, 1934, by K. J. Kadow from a pond in the peach orchard owned by E. C. Riechman and located 2340′ S. of the N. E. corner of Sec. 23–T. 1S–R. 1W., R.F.D., Irvington, Washington County, Ill.

LABORATORY No. 80815

Determinations made

	Parts per million
Iron (Fe)	
Filtered	Trace
Unfiltered	15.0
Manganese (Mn)	0
Silica (SiO_2)	1.0
Turbidity	1000.0
Calcium (Ca)	9.0
Magnesium (Mg)	.4
Ammonium (NH_4)	.5
Sodium (Na)	43.7
Sulfate (SO_4)	75.2
Nitrate (NO_3)	2.0
Chlorid (Cl)	8.0
Alkalinity as $CaCO_3$	
Phenolphthalein	0
Methyl orange	30.0
Residue	168.0
Total hardness	24.5

Hypothetical combinations

	Parts per million	*Grams per gallon*
Sodium nitrate ($NaNO_3$)	2.6	.15
Sodium chlorid (NaCl)	13.4	.78
Sodium sulfate (Na_2SO_4)	110.9	6.46
Sodium carbonate (Na_2CO_3)	4.2	.25
Ammonium carbonate ($(NH_4)_2CO_3$	1.4	.08
Magnesium carbonate ($MgCO_3$)	1.7	.10
Calcium carbonate ($CaCO_3$)	22.5	1.31
Silica (SiO_2)	1.0	.05
Totals	157.7	9.18

STATE WATER SURVEY DIVISION
C. S. BORUFF, *Chemist*

March 16, 1934

SPRAY SCHEDULE No. 1.—PEACH EXPERIMENTS AT C. J. THOMAS ORCHARD, CARBONDALE, ILLINOIS, 1932[a]

Plots	Materials in early-season sprays	Early-season sprays applied					
		Shuck	2d	3d	4th	5th	6th
1, 13	Zinc-lime-lead 8-8-4-100	x	x	x	x	...	...
	Zinc-lime 8-8-100	...	...	...	...	x	x
2, 14	Zinc-lime-lead 4-4-4-100	x	x	x	x	...	...
	Zinc-lime 4-4-100	...	...	...	...	x	x
3, 15	Zinc-lime-lead 4-8-4-100	x	x	x	x	...	...
	Zinc-lime 4-8-100	...	...	...	...	x	x
4, 16	Zinc-lime-lead 2-4-4-100	x	x	x	x	...	...
	Zinc-lime 2-4-100	...	...	...	...	x	x
5	Zinc-lime-lead 1-4-4-100	x	x	x	x	...	...
	Zinc-lime 1-4-100	...	...	...	...	x	x
6, 9	Lime-lead 16-4-100	x	x	x	x	...	...
7, 18	Lime-lead 8-4-100	x	x	x	x	...	...
8	Lime-lead 4-4-100	x	x	x	x	...	...
17	Lead 4-100	x	x	x	x	...	...
17a	Absolute check	...	...	...	...	...	...
10, 19	Zinc-lime 8-8-100	x	x	x	x	x	x
Check 1	Absolute check	...	...	...	...	...	...
Check 2	Zinc-lime-lead 8-8-3-100	x	x	x	x	...	...
11	Lead-lime 3-6-100	x	x	x	x	...	...
	Flotation paste 12-100	...	x	x	x	...	...

Plot	Late-season sprays		
	Materials	1st	2d
1	Kolofog 10-100	x	x
2	Dritomic 6-100	x	x
3	Flotation sulfur paste 12-100	x	x
4	Flotation sulfur dry 6-100	x	x
5	Sulfur dust, 300-mesh	80%	80%
	Lime	20%	20%
6	Sulfur dust, 300-mesh	80%	80%
	Lime	20%	20%
	Oil (by weight)	5%	5%
9	Flotation sulfur dust	25%	25%
	300-mesh sulfur	55%	55%
	Lime	20%	20%
7	Flotation sulfur dust	80%	80%
	Lime	20%	20%
8	Flotation sulfur dust	45%	45%
	300-mesh sulfur	35%	35%
	Li e	20%	20%
17a	No treatment	....	....
10	Flotation sulfur dust	25%	25%
	300-mesh sulfur	55%	55%
	Lime	20%	20%
	Oil (by weight)	5%	5%
Check 1		....	....
Check 2		....	....

[a]Cooperative experiment by Department of Horticulture and Illinois State Natural History Survey. Sprays applied at two-week intervals beginning April 25 to 27, 1932. Fungicidal sprays applied three weeks and one week before harvest.

SPRAY SCHEDULE No. 2—PEACH EXPERIMENTS AT UNIVERSITY FARM, OLNEY, ILLINOIS, 1933[a]

Plot	Spray materials used	Early-season sprays applied					Late-season sprays
		Shuck	2d	3d	4th	5th	
							number
1....	Absolute check, no sprays or dusts..	...	...	...	...	...	....
2....	Lead-lime 3-6-100.....	x	x	x	x	x	....
	Flotation sulfur 6-100,.....	...	...	...	...	...	1
3....	Lead-lime-zinc 3-8-8-100.....	x	x	x	x	x	....
	Flotation sulfur 6-100.....	...	...	...	...	...	1

[a]Sprays were applied at about two-week intervals. Trees were five years old, in good vigor, and well cared for. Each plot had Elberta and Gage varieties in it.

SPRAY SCHEDULE No. 3.—PEACH EXPERIMENTS AT E. C. RIECHMAN ORCHARD, IRVINGTON, ILLINOIS, 1933[a]

Plot	Spray materials used	Early-season sprays applied					Late-season sprays
		Shuck	2d	3d	4th	5th	
1....	Absolute check, no sprays or dusts..	...	...	...	...	...	....
2....	Lead-lime 3-6-100.....	x	x	x	x	x	....
3....	Lead-lime-zinc 3-8-8-100.....	x	x	x	x	x	....
4....	Lead-lime-zinc 3-8-4-100.....	x	x	x	x	...	....
5....	Lime-zinc 8-8-100.....	x	x	x	x	x	....

[a]Sprays were applied at about two-week intervals. Orchard rather low in vigor with general infections of peach scab and bacterial spot. All trees in the experiment were Elbertas.

SPRAY SCHEDULE No. 4.—PEACH EXPERIMENTS AT URBANA, ILLINOIS, 1934[a]

Plot	Spray materials used	Early-season sprays applied					Late-season sprays
		Shuck	2d	3d	4th	5th	
1....	Absolute check, no sprays or dusts..	...	...	...	...	...	....
2....	Lead-lime 3-6-100.....	x	x	x	x	x	....
3....	Lead-lime-zinc 3-8-8-100.....	x	x	x	x	x	....

[a]Sprays were applied at about two-week intervals. Orchard in good vigor, on Carrington silt loam soil. Very little bacterial spot. All trees in the experiment were Elbertas.

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